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⑯ Stable pourable aqueous bleaching compositions comprising solid organic peroxy acids and at least two polymers.

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EP-A- 0 201 958
EP-A- 0 254 331
EP-A- 0 283 792
EP-A- 0 301 882
GB-A- 1 535 804

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⑯ Proprietor : **AKZO N.V.**
Velperweg 76
NL-6824 BM Arnhem (NL)

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⑯ Inventor : **Torenbeek, Reinder**
Quabbenburgerweg 8
NL-7396 NN Terwolde (Gld.) (NL)
Inventor : **Ploumen, Jan Joseph Hubert**
Florasvingel 79
NL-6043 WC Roermond (NL)

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⑯ References cited :
EP-A- 0 160 342
EP-A- 0 176 124
EP-A- 0 200 163

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Description

The invention relates to pourable bleaching compositions comprising a solid, substantially water-insoluble organic peroxy acid stably suspended in an aqueous medium. In particular, the present invention relates to bleaching compositions of the above type characterized in that the aqueous medium also comprises at least two polymers wherein the first polymer is one or more natural gums, preferably xanthan gum, and the second polymer is selected from the group consisting of polyvinyl alcohol, cellulose derivatives and mixtures thereof. The bleaching composition may additionally be comprised of an electrolyte, such as Na₂SO₄.

The bleaching compositions of the current invention may be used alone or in combination with other bleaches. Additionally, the current bleaching compositions may be included as part of detergent, bleaching, cleaning and/or disinfecting formulations.

Bleaching compositions comprising a solid, substantially water-insoluble organic peroxy acid stably suspended in an aqueous medium are generally known from British Patent Specification 1 535 804. It claims fabric bleaching compositions having a viscosity from 0,2 to 100 Pa.s (200 to 100,000 cp.) and a non-alkaline pH, the compositions comprising an aqueous carrier, 1-40 weight % particulate organic substantially water-insoluble peroxygen compound and a thickening agent. Specifically mentioned thickening agents are inorganic thickeners, such as clays, and organic thickeners, such as water-soluble gums, mucilaginous materials, starches, polyacrylamides and carboxylic polymethylene. In particular, British Patent Specification 1 535 804 discloses the use of cellulose derivatives such as carboxymethyl celluloses, hydroxypropyl cellulose and methyl hydroxybutyl cellulose, hydrolyzed proteins such as hydrolyzed keratins, glutens, polyvinyl alcohol and polyvinylpyrrolidone, and natural gums such as gum arabic, carrageen and various agars.

Further, the non-prepublished European Patent Application No. 283 792 discloses storage-stable, pourable aqueous bleach suspensions having a pH value in the range of 1 to 6 and containing (a) particulate, water-insoluble peroxy-carboxylic acid (e.g., diperoxydodecanedioic acid), (b) xanthan gum or agar, (c) hydratable neutral salt (e.g., Na₂SO₄), (d) optionally an acid for pH regulation (e.g., H₂SO₄), and (e) aqueous liquid.

It is known to be advantageous to use liquid bleaching compositions rather than solid bleaching compositions in automatic clothes washers and dryers. Among those advantages is that with liquid bleaching compositions there is no need for cost-increasing shaping steps, such as granulating and drying. Additionally, liquid bleaching compositions are more easily dispersed in wash liquor or in an automatic clothes dryer so the fabrics are more rapidly and evenly bleached. Uneven bleaching can damage fabric as a result of localized high concentrations of bleaching agent.

As disclosed in European Patent Application 176 124, the bleaching compositions of GB 1 535 804, at least as far as they are pourable, have the disadvantage that they are not physically stable. As shown by Composition 7 in EP 176 124, after prolonged storage, pourable bleaching compositions of GB 1 535 804 undergo phase separation, producing a thick bottom layer which is difficult to disperse or homogenize. Consequently, the aforementioned advantage of even fabric distribution may be partly eliminated.

Further it should be mentioned that GB 1 535 804 does not disclose or suggest the use of more than one thickening agent in a single fabric bleaching composition. Indeed, it is clear from Example III of GB 1 535 804 that the cellulose derivatives tested as thickening agents were tested in individual, separate bleach compositions. Additionally, the bleach composition of Example III of GB 1 535 804 is a "thick, semi-gelatinous composition" (see page 11, lines 32-35 of GB 1 535 804) rather than a pourable composition of the present invention.

It should be noted that United States Patent 4 232 141 (NL 707 916) discloses, *inter alia*, grinding coarser particles of a polymerization initiator in an aqueous medium containing a dispersing agent to form an aqueous dispersion of the polymerization initiator. The polymerization initiator may be, *inter alia*, a peroxy dicarbonate or a benzoyl peroxide. Claim 9 claims that the dispersing agent may be polyvinyl alcohol, cellulose ether, gelatine or a mixture thereof. However, only single dispersing agents (either polyvinyl alcohol or methyl cellulose) are used in the working examples of US 4 232 141 to form polymerization initiator dispersions. These dispersions were then added to vinyl chloride polymerization suspensions to form polyvinyl chloride. Some vinyl chloride polymerization suspensions of the examples of US 4 232 141 contain a mixture of polyvinyl alcohol and methyl cellulose. However, as demonstrated herein below, an aqueous suspension acceptable under bleaching conditions (pourability, physical stability and chemical stability) and prepared as suggested by US 4 232 141 is not physically stable.

The bleaching compositions of the current application are physically stable when the compositions undergo insignificant, and preferably no, phase separation during a reasonable storage time.

The solid, substantially water-insoluble organic peroxy acids which may be used in the bleaching compositions of the current invention are generally known in the art. As non-limiting examples, the solid organic peroxy acids disclosed in European Patent Applications 160 342, 176 124 and 267 175, US Patents 4 681 592 and 4 634 551 and GB Patent Specification 1 535 804 may be used and are all herein incorporated by reference.

The most preferred organic peroxy acids which may be used in the compositions of the current invention are (1) diperoxy acids, such as 1,12-diperoxydodecanedioic acid ("DPDA"), diperazelaic acid and 1,13 diperoxytridecanoic acid, (2) peroxy acids which have a polar amide link in the hydrocarbon chain, such as N-decanoyl-6-amino-peroxyhexanoic acid, N-dodecanoyl-6-aminoperoxyhexanoic acid, 4-nonylamino-4-oxoperoxybutyric acid and 6-nonylamino-6-oxoperoxyhexanoic acid, and (3) alkyl sulphonyl peroxycarboxylic acids, such as heptyl sulphonyl perpropionic acid, octyl sulphonyl perpropionic acid, nonyl sulphonyl perpropionic acid and decyl sulphonyl perpropionic acid. Methods for preparing such preferred organic peroxy acids are known in the art and in particular from the above cited references. Optionally, the solid organic peroxy acid may be coated with a water-impermeable material, such as the fatty acids lauric acid, myristic acid and mixtures thereof, as known from European Patent Application 254 331. The amount of organic peroxy acid in the current bleaching formulations depends on criteria such as the active oxygen ("A.O.") content of the peroxy acid and the intended use of the bleaching composition. The preferred amount of peroxy acid is that which will provide effective washing, bleaching, cleaning and/or disinfecting in a diluted use liquor. Generally, though non-limiting, the current bleaching compositions have a peroxy acid concentration which will provide an A.O. content of between about 1 and about 200 ppm, and preferably between about 2 and about 100 ppm in a typical diluted liquor for use in washing, bleaching, cleaning and/or disinfecting.

The first polymer is one or more natural gums. As non-limiting examples, the natural gums may be xanthan gum, guar gum, gum arabic, carrageen and agars obtained from seaweed. Xanthan gum is the preferred natural gum. The amount of natural gum desired in the current bleaching formulations is the amount which is effective to provide a physically and chemically stable, pourable aqueous formulation. Generally, though non-limiting, natural gum is present as about 0.1 to about 1 wt.% of the bleaching composition.

The second polymer is selected from the group consisting of polyvinyl alcohol, one or more cellulose derivatives and mixtures thereof. A group of cellulose derivatives particularly useful are cellulose ethers. Cellulose ethers are known from, for example, Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition, Vol. A5, pages 461-487. Of particular use in the current bleaching compositions are methyl cellulose, methyl hydroxypropyl cellulose, methyl hydroxybutyl cellulose, hydroxyethyl cellulose and carboxymethyl cellulose. The amount of second polymer incorporated in the current bleaching formulations is the amount which will provide a physically and chemically stable, pourable aqueous bleaching composition. Generally, though non-limiting, the second polymer is present as about 0.02 to about 2 wt.% of the bleaching composition.

An electrolyte may also be present in the aqueous medium to help provide a useful, pourable bleaching composition. The electrolyte may result from the residual acid present in the peroxy acid as a result of the peroxidation reaction. The electrolyte may also be added deliberately to enhance the physical stability of the current suspensions and increase their safe handling (See European Patent Application 176 124). Examples of suitable electrolytes are Na_2SO_4 , K_2SO_4 , MgSO_4 , $\text{Al}_2(\text{SO}_4)_3$, NaNO_3 and borate salts. The amount of electrolyte present depends, *inter alia*, on the peroxy acid and the polymers employed and on the intended use of the suspension. However, in general, though non-limiting, the electrolyte may be up to about 30 wt.% of the composition.

Optionally, the current bleaching compositions may also comprise antifreezing agents, such as glycol. The bleaching compositions of the current invention are further illustrated by the following non-limiting examples.

Example 1 (Comparative Example)

This example illustrates the problems presented by aqueous organic peroxy acid suspensions which contain no polymer or which contain only one water-soluble polymer. Test suspensions of 500 grams were prepared by mixing 274 grams organic peroxy acid (1,12-diperoxydodecanedioic acid ("DPDA")) in wet filter cake form, having an active oxygen (A.O.) content of 5.47% with a solution of 15 grams Na_2SO_4 and 1 gram test polymer (if present) based on active material in 210 grams water. This produced test suspensions having an active oxygen content of 3.0%. The viscosity of each test suspension was measured (Brookfield RV, 20 rev/min) and the physical stability (in terms of phase separation) was monitored during an 8 week 20°C storage period. The results are contained in Table 1.

Table 1

5	<u>Test Suspension</u>	<u>Water-soluble Polymer</u>	<u>Viscosity (mPa.s)</u>	<u>Phase Separation</u>
10	1A	None	2400	None
15	1B	Xanthan gum (Rhodigel 23 from Rhone Poulenc)	1700	Small amount
20	1C	Hydroxyethyl cellulose (Natrosol 250 L from Hercules)	50	Large amount

As shown in the results in Table 1, even though the addition of the water-soluble polymer hydroxyethyl cellulose substantially reduces the test suspension viscosity, making it conveniently pourable, the phase separation is unacceptable. The addition of xanthan gum alone to the test suspension reduces viscosity, but not enough to provide acceptable pourability. Also, Test Suspension 1B is not physically stable as indicated by the phase separation.

Example 2

To have use as a bleaching composition, the suspensions of the current invention must be chemically stable as well as pourable and physically stable. That is, the bleaching compositions of the current invention must retain their ability to bleach while they are being stored prior to use. The chemical stability of a peroxy acid is indicated by the retention of active oxygen (A.O.). However, active oxygen is affected by the presence of H₂O₂ as well as peroxy acid (such as DPDA). H₂O₂ is formed by the decay reactions of peroxy acids. Therefore, a more accurate indication of chemical stability after storage is the "residual peroxy acid", or in this case, "residual DPDA". "Residual DPDA" is the active oxygen content (A.O.) minus H₂O₂ formed by the decay of the peroxyacid. The H₂O₂ content was determined by extraction with a mixture of diethyl ether and water, separation of the water layer, addition of Ti(IV) reagent and spectrophotometric measurement of the yellow complex formed.

Two 500 gram test suspensions were independently prepared by mixing 274 grams DPDA filter cake (A.O. = 5.47%) in about 200 grams of water. The first suspension was completed by adding 15 grams Na₂SO₄ and 0.25 gram Dequest 2010 (a sequestering agent available from Monsanto). The second suspension was completed by adding 15 grams Na₂SO₄, 0.25 grams Dequest 2010, 1 gram hydroxyethyl cellulose (Natrosol 250 L) and 1 gram xanthan gum (Rhodigel 23). The initial active oxygen content and viscosity of each suspension were measured. Each suspension was divided in half. One-half of each suspension was stored for 8 weeks at 20°C and the other half stored for 8 weeks at 30°C. The chemical stability (active oxygen loss and residual DPDA), the rheology (viscosity) and the physical stability (phase separation) data are in Table 2 below.

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Table 2

5	Suspension Without Polymers (Suspension 2A)	Suspension With Xanthan Gum and Hydroxyethyl Cellulose (Suspension 2B)
10		
15	Loss in Active Oxygen (8 weeks at 30 C)	< 1% 99% 96%
20	Residual DPOA After 8 weeks at 20 C After 8 weeks at 30 C	98% 95%
25	Phase Separation After 8 weeks at 20 C After 8 weeks at 30 C	none none
30	Viscosity (Brookfield) RV, 10 rev/min) in mPa.s Initially After 8 weeks at 20 C	9500 650 . 9800 580
35		
40	Surprisingly, the suspensions of the current invention were conveniently pourable as well as being chemically and physically stable over the 8 week test period.	
45	In order to compare and predict the rheological behavior ("pourability") of known compositions and compositions of the current invention, a plot of viscosity vs. shear rate ("rheogram") was generated for Test Suspensions 1B and 1C of Example 1 and for the suspensions of Example 2. The shear stress was recorded versus the shear rate applied with a Haake Rotovisco RV 100 at 20°. The calculated viscosity values are plotted versus the shear rate in Fig. 1. Suspensions which follow the curve of Suspension 1B are not easily pourable as demonstrated by laboratory attempts to pour them without shaking the contents of the container. (Note that such lack of pourability was also indicated by the Brookfield viscosity measurement of Suspension 1B as reported at Table 1.) However, suspensions which follow the curve of Suspension 2B are pourable. Liquid detergents currently available in Western Europe (therefore having commercially acceptable pourability) follow the curve of Suspension 2B and are of lower viscosity than Suspension 1B. As discussed in Example 1, Suspension 1C is pourable but not physically stable.	
50	Additionally, from plots of shear stress versus shear rate, the yield value of Suspension 2A was found to be about 200 Pa while that of Suspension 2B was found to be about 15 Pa. For suspensions of the current invention, yield values between about 5 and about 20 Pa provide the most desirable "pourability" behavior.	
55	<u>Example 3 (Comparative Example)</u> A blaching composition comprised of components suggested by the disclosure in US Patent 4 232 141 was prepared as a comparative example. A test suspension was prepared by mixing 326.1 grams DPDA w t filter cake (A.O. = 5.22%) with 193.9 grams of an aqueous solution of 0.25 gram D qu st 2010, 1.0 gram PVA	

(Gohsenol KP-08, 75% hydrolyzed, available from Nippon Gohsei) and 1.0 gram hydroxyethyl cellulose (Natosol 250 L available from Hercules). This produced a test suspension having an active oxygen content of 3.3%. Sodium sulfate was omitted from the composition since PVA precipitated from solution in the presence of Na₂SO₄ prior to the addition of DPDA. The viscosity of the test suspension was 89 mPa.s (Brookfield LVT, 30 rev/min). After 8 weeks storage at 20°C, 160 ml of water separated from the test suspension.

5 Example 4

A bleaching composition was prepared in accordance with the composition of Example 3 modified by the addition of 1.0 gram xanthan gum, placing the test suspension of this Example 4 within the scope of the current invention. The viscosity of the test suspension was 938 mPa.s (Brookfield LTV, 30 rev/min). After 8 weeks storage at 20°C, only an insignificant 4 ml of water separated from the test suspension. The composition was conveniently pourable.

15 Example 5

As disclosed in European Patent Application 254 331, organic peroxy acids may be prepared in such a manner that the resulting organic peroxy acid also comprises a water-impermeable material, such as fatty acid. The fatty acid may, among other things, increase the safe handling and use of organic peroxy acids.

20 Test suspensions using DPDA with lauric acid (a fatty acid) were prepared by mixing 206 grams DPDA coated with lauric acid (wet filter cake, A.O. = 6.07%) aqueous solutions containing varying amounts PVA or PVA and xanthan gum as set forth in Table 3 to form 500 gram aqueous suspensions. The lauric acid-coated DPDA was prepared substantially in accordance with the method of European Patent Application 254 331 by heating and stirring a suspension of DPDA at 50°C, adding lauric acid in a weight ratio of 3:1 DPDA to lauric acid, stirring for 10 minutes, cooling and separating the DPDA and lauric acid combination from water on a filter.

Again, the viscosity of each test suspension was measured (Brookfield RV at 20 rev/min, except Test Suspension 3D which was measured at Brookfield LV at 60 rev/min) and the physical stability was monitored during an 8 week period at 20°C. The data are reported in Table 3.

30 Test Suspension 3A does not contain a water-soluble polymer. It does not separate over the 8 week period but it is not conveniently pourable. Test Suspensions 3B, 3C and 3D contain the water-soluble polymer PVA (as suggested by US Patent 4 232 141). They are conveniently pourable but have unacceptable phase separation. Test Suspension 3E, containing both xanthan gum and PVA according to the present invention, shows no phase separation, is as chemically stable as Test Suspension 3A and is conveniently pourable. Thus, the current bleaching compositions are suitable for use with organic peroxy acids which also comprise a water-impermeable material.

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Table 3

<u>Test Suspension</u>	<u>Water-soluble Polymer</u>	<u>Viscosity (mPa.s)</u>	<u>H₂O Separation After 8 weeks</u>
3A	None	7600	0
3B	0.5 g PVA (Gohsenol KP-08)	905	38
3C	1.0 g PVA (Gohsenol KP-08)	421	42
3D	2.0 g PVA (Gohsenol KP-08)	43	139
3E	1.0 g PVA (Gohsenol KP-08) and 1.0 g xanthan gum (Rhodigel)	1360	0

Example 6

For some purposes (such as bulk transportation), it is desirable to produce aqueous, pourable suspensions having relatively high peroxy acid concentration and/or active oxygen content. It has been surprisingly found that the bleaching compositions of the current invention are capable of containing a substantially increased amount of organic peroxy acid on a weight percent basis.

For example, currently known aqueous suspensions of the organic peroxy acid DPDA are capable of a maximum of about 32 wt.% DPDA and have an active oxygen content of about 3.5%. In the case of aqueous suspensions of DPDA in combination with a water-impermeable material, such as a fatty acid (for example, lauric acid), the active oxygen content may be reduced to about 2.5%. Surprisingly, aqueous suspensions have been prepared using the polymer system of the current invention to produce bleaching compositions with substantially increased DPDA (with and without lauric acid) concentration and a substantially increased active oxygen content. The details of these compositions are contained in Table 4.

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Table 4

		Suspension of DPDA Particles	Suspension of DPDA-Lauric Acid Particles
10	1. Composition (wt.%)		
	DPDA	43.5	-
	DPDA-Lauric Acid (3:1)	-	40.7
	Hydroxyethyl cellulose (Natrosol 250 L)	0.3	-
15	Polyvinyl Alcohol (Gohsenol KP-08)	-	0.4
	Xanthan Gum (Rhodigel)	0.1	0.2
20	Dequest 2010	0.05	0.05
	2. Initial A.O. content of DPDA (%)	11.5	8.6
25	3. Initial A.O. content of Suspension	5.0	3.5
	4. Chemical Stability		
30	8 weeks, 20 C (Residual DPDA as % of Initial DPDA)	96	98
	8 weeks, 30 C (Residual DPDA as % of Initial DPDA)	95	97
35	5. Phase Stability		
40	8 weeks, 30 C	No Phase Separation	No Phase Separation

Example 7

45 Suspensions having relatively high peroxy acid concentrations (e.g., above about 20 wt.% for peroxyacids such as DPDA) are preferred for industrial purposes, such as bulk transportation and handling. However, relatively low peroxy acid concentrations (e.g., about 5-10 wt.% for peroxyacids such as DPDA for U.S. consumers) are desirable for household use. Therefore, it is most preferable that the previously described pourable, storage-stable concentrated suspensions can be diluted to form pourable, storage-stable dilute suspensions.

50 As provided in Table 5, two suspensions having relatively high peroxy acid concentrations (27 wt.%) were prepared. Suspension 5A is a comparative example containing peroxy acid and sodium sulfate. Suspension 5B is a two polymer formulation within the current invention. Comparative Suspension 5A was used to prepare 500 ml dilut. Comparative Suspension 5C. Suspension 5B was used to prepar 500 ml dilute Suspension 5D according to the current inv ntion. As r port d in Tabl 5, dilute Suspension 5D is physically and chemically stabl over a 4 week period whil Susp nsion 5C s parates after 3 weeks at 40°C. Chemical stability is r ported in terms of "R esidual DPDA". "R esidual DPDA" was determined by the method d scribd in Example 2, above.

Table 5

5	10	Test Suspension*	Water-Soluble Polymer(s)	Wt.% DPDA	Phase Stability (Separate Water Phase After 4 weeks, 40°C)	Chemical Stability (Residual DPDA After 4 weeks, 40°C)
15	5A	-	None	27	Not Determined	Not Determined
20	5B	-	0.2 wt.% xanthan gum 0.2 wt.% hydroxyethyl cellulose	27	Not Determined	Not Determined
25	5C	3	0.5 wt.% xanthan gum	6	50 ml	90%
30	5D	3	0.05 wt.% xanthan gum 0.05 wt.% hydroxyethyl cellulose	6	0 ml	90%

* All Test Suspensions contain 3 wt.% sodium sulfate. Test suspensions 5C and 5D contain 0.5 wt.% Dequest 2010 (a sequestering agent) and 3 wt.% acid.

Example 8

- 50 This Example 8 demonstrates, *inter alia*, the effect of temperature on suspensions of the current invention. Temperature effects are particularly important in that industrial processing and transportation is likely to occur at lower temperatures (e.g., about 10°C-30°C) while consumer storage and usage is likely to occur at higher temperatures (e.g., about 20°-40°C).
- 55 Test suspensions identical to those of Example 2 were prepared. Suspension 8A is identical to Suspension 2A. Suspension 8B is identical to Suspension 2B. Portions of the suspensions were stored for 8 weeks at 20°C, 30°C and 40°C then tested for chemical stability (residual DPDA), phase stability and rheological stability ("pourability"). Additionally, these characteristics were also monitored after 4 weeks for suspensions stored at 40°C. The results are provided in Table 6. It should be noted that "pourability" was determined by pouring (or

attempting to pour) each suspension from a 500 ml container. Suspensions giving a streaming behavior similar to that of commercially available heavy duty detergents were "pourable".

Table 6

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Chemical Stability
(Residual DPDA)

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		Suspension 8A <u>(Without Polymers)</u>	Suspension 8B <u>(With Polymers)</u>
a.	8 weeks/20°C	99%	98%
b.	8 weeks/30°C	96%	95%
c.	4 weeks/40°C	93%	92%
d.	8 weeks/40°C	84%	79%

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Phase Stability

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a.	8 weeks/20°C	No Phase Separation	No Phase Separation
b.	8 weeks/30°C	" "	" "
c.	4 weeks/40°C	" "	" "
d.	8 weeks/40°C	" "	" "

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Rheological Stability

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a.	8 weeks/20°C	Not Pourable	Pourable
b.	8 weeks/30°C	" "	"
c.	4 weeks/40°C	" "	"
d.	8 weeks/40°C	" "	Pourable (but thickening)

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Analysis of the data provided in Table 6 indicates that the suspensions of the current invention are chemically, physically and rheologically stable over time and temperature. Additionally, the chemical stability and physical stability of the suspension of the current invention (Suspension 8B) are equal, or substantially equal, to those of Suspension 8A while Suspension 8B has the advantage of rheological superiority and stability.

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Claims

Claims for the following contracting States : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

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1. A pourable bleaching composition comprising a solid, substantially water-insoluble organic peroxy acid stably suspended in an aqueous medium characterized in that the aqueous medium also comprises at least two polymers wherein the first polymer is one or more natural gums and the second polymer is selected from the group consisting of polyvinyl alcohol, one or more cellulose derivatives, and mixtures thereof.

2. A composition according to claim 1, characterized in that the first polymer is xanthan gum.
3. A composition according to any one of the preceding claims characterized in that the second polymer is one or more cellulose ethers.
5. 4. A composition according to any one of the preceding claims, characterized in that the second polymer is selected from the group methyl cellulose, methyl hydroxypropyl cellulose, methyl hydroxybutyl cellulose, hydroxyethyl cellulose and carboxymethyl cellulose.
10. 5. A composition according to any one of the preceding claims, characterized in that the organic peroxy acid is further comprised of a water-impermeable material.
6. The composition according to the preceding claim 5, characterized in that the water-impermeable material is selected from the group consisting of lauric acid, myristic acid and a mixture thereof.
15. 7. A composition according to any one of the preceding claims characterized in that the composition further comprises an electrolyte.
8. A composition according to the preceding claim 7 characterized in that the electrolyte is sodium sulfate.
20. 9. A composition according to any of the preceding claims, characterized in that the organic peroxy acid is a dperoxy acid.
10. 10. A composition according to claim 9, wherein the dperoxy acid is 1,12-dperoxydodecanedioic acid.
25. 11. A composition according to any one of the claims 1-8 characterized in that the organic peroxy acid has a polar amide link in the hydrocarbon chain.
12. A composition according to any one of the claims 1-8 characterized in that the organic peroxy acid is an alkyl sulphonyl peroxycarboxylic acid.
30. 13. A detergent, bleaching, cleaning and/or disinfecting formulation comprising a bleaching composition according to any one of the preceding claims.

Claims for the following contracting State : ES

35. 1. A process for making a pourable bleaching composition comprising a solid, substantially water-insoluble organic peroxy acid stably suspended in an aqueous medium which contains at least two polymers wherein the first polymer is one or more natural gums and the second polymer is selected from the group consisting of polyvinyl alcohol, one or more cellulose derivatives, and mixtures thereof.
40. 2. A process according to claim 1, characterized in that the first polymer is xanthan gum.
3. A process according to any one of the preceding claims characterized in that the second polymer is one or more cellulose ethers.
45. 4. A process according to any one of the preceding claims, characterized in that the second polymer is selected from the group methyl cellulose, methyl hydroxypropyl cellulose, methyl hydroxybutyl cellulose, hydroxyethyl cellulose and carboxymethyl cellulose.
50. 5. A process according to any one of the preceding claims, characterized in that the organic peroxy acid is further comprised of a water-impermeable material.
6. The process according to the preceding claim 5, characterized in that the water-impermeable material is selected from the group consisting of lauric acid, myristic acid and a mixture thereof.
55. 7. A process according to any one of the preceding claims characterized in that the composition further comprises an electrolyte.
8. A process according to the preceding claim 7 characterized in that the electrolyte is sodium sulfate.

9. A process according to any of the preceding claims, characterized in that the organic peroxy acid is a diperoxy acid.
10. A process according to claim 9, wherein the diperoxy acid is 1,12-diperoxydodecanedioic acid.
- 5 11. A process according to any one of the claims 1-8 characterized in that the organic peroxy acid has a polar amide link in the hydrocarbon chain.
- 10 12. A process according to any one of the claims 1-8 characterized in that the organic peroxy acid is an alkyl sulphonyl peroxycarboxylic acid.
13. A process of using the composition made by a process in accordance with claims 1-12 as a detergent, bleaching, cleaning and/or disinfecting formulation.

15 **Patentansprüche**

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

1. Giessfähiges Bleichmittel enthaltend eine feste, im wesentlichen wasserunlösliche organische Peroxsäure, die stabil in einem wässrigen Medium suspendiert ist, dadurch gekennzeichnet, dass das wässrige Medium ausserdem mindestens zwei Polymere enthält, wobei das erste Polymer ein natürlicher Gummi oder mehrere natürliche Gummi und das zweite Polymer gewählt ist aus der Gruppe bestehend aus Polyvinylalkohol, einem oder mehreren Cellulosederivat(en) und Mischungen hiervon.
2. Mittel nach Anspruch 1, dadurch gekennzeichnet, dass das erste Polymer Xanthangummi ist.
3. Mittel nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das zweite Polymer ein oder mehrere Celluloseether ist bzw. sind.
4. Mittel nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das zweite Polymer gewählt ist aus der Gruppe Methylcellulose, Methylhydroxypropylcellulose, Methylhydroxybutylcellulose, Hydroxyethylcellulose und Carboxymethylcellulose.
5. Mittel nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die organische Peroxsäure ausserdem ein wasserundurchlässiges Material enthält.
6. Mittel nach Anspruch 5, dadurch gekennzeichnet, dass das wasserundurchlässige Material gewählt ist aus der Gruppe bestehend aus Laurinsäure, Myristinsäure und Mischungen hiervon.
7. Mittel nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das Mittel ausserdem einen Elektrolyt enthält.
8. Mittel nach Anspruch 7, dadurch gekennzeichnet, dass der Elektrolyt Natriumsulfat ist.
9. Mittel nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die organische Peroxsäure eine Diperoxysäure ist.
10. Mittel nach Anspruch 9, bei welcher die Diperoxysäure 1,12-Diperoxydodecanösäure ist.
11. Mittel nach einem der vorangehenden Ansprüche 1-8, dadurch gekennzeichnet, dass die organische Peroxsäure in der Kohlenwasserstoffkette eine polare Amidbrücke enthält.
- 50 12. Mittel nach einem der Ansprüche 1-8, dadurch gekennzeichnet, dass die organische Peroxsäure eine Alkylsulfonylperoxycarbonsäure ist.
13. Wasch-, Bleich-, Reinigungs- und/oder Desinfektions-Zusammensetzung enthaltend in Bleichmittel gemäß einem der vorangehenden Ansprüche.

Patentansprüch für folgend n V rtragsstaat : ES

1. Verfahren zur Herstellung eines giessfühigen Blasenmittels enthaltend ein festes, im wesentlichen wasserunlösliche organische Peroxsüre, die stabil in einem wüssrigen Medium suspendiert ist, dadurch gekennzeichnet, dass das wüssrige Medium auüerdem mindestens zwei Polymere enthült, wobei das erste Polymer ein natülicher Gummi oder mehrere natürliche Gummie und das zweite Polymer gewühlt ist aus der Gruppe bestehend aus Polyvinylalkohol, einem oder oder mehreren Cellulosederivat(en) und Mischungen hiervon.
- 10 2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das erste Polymer Xanthangummi ist.
3. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das zweite Polymer ein oder mehrere Celluloseether ist bzw. sind.
- 15 4. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das zweite Polymer gewühlt ist aus der Gruppe Methylcellulose, Methylhydroxypropylcellulose, Methylhydroxybutylcellulose, Hydroxyethylcellulose und Carboxymethylcellulose.
5. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die organische Peroxsüre auüerdem ein wasserundurchlüssiges Material enthült.
- 20 6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, dass das wasserundurchlüssige Material gewühlt ist aus der Gruppe bestehend aus Laurinsüre, Myristinsüre und Mischungen hiervon.
7. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das Mittel auüerdem einen Elektrolyt enthült.
- 25 8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, dass der Elektrolyt Natriumsulfat ist.
9. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die organische Peroxsüre eine Diperoxsüre ist.
- 30 10. Verfahren nach Anspruch 9, bei welcher die Diperoxsüre 1,12-Diperoxydodecanisüre ist.
11. Verfahren nach einem der vorangehenden Ansprüche 1-8, dadurch gekennzeichnet, dass die organische Peroxsüre in der Kohlenwasserstoffkette eine polare Amidbrücke enthült.
- 35 12. Verfahren nach einem der Ansprüche 1-8, dadurch gekennzeichnet, dass die organische Peroxsüre eine Alkylsulfonylperoxycarbonüre ist.
13. Verfahren zur Verwendung des Mittels hergestellt mittels eines Verfahrens nach Ansprüchen 1-12 als Wasch-, Bleich-, Reinigungs- und/oder Desinfektions-Zusammensetzung.
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Revendications

- 45 **Revendications pour les Etats contractants suivants : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE**

1. Une composition de blanchiment &coulable, comprenant un peroxyacide organique solide, sensible insoluble dans l'eau, en suspension stable dans un milieu aqueux, caractérisée en ce que le milieu aqueux comprend aussi au moins deux polymères, le premier polymère consistant en une ou plusieurs gommes naturelles et le second polymère &tant choisi dans le groupe comprenant l'alcool polyvinyle, un ou plusieurs dérivés de cellulose, et leurs mélanges.
- 50 2. Une composition selon la revendication 1, caractérisée en ce que le premi &er polymère est la gomme xanthane.
3. Une composition selon l'un quelconque des revendications prêcedentes, caractérisé en ce que le second polymère est un ou plusieurs ðers de cellulose.
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4. Une composition selon l'une quelconque des revendicati ns précédentes, caractérisée en ce qu le se-
cond polymère est choisi dans le groupe comprenant: méthylcellulose, méthylhydroxypropylcellulos , mé-
thylhydroxybutylcellulose, hydroxyéthylcellulose et carboxyméthyl cellulose.
5. Une composition selon l'une quelconque des revendications précédentes, caractérisée en ce que le pe-
roxyacide organique comprend de plus un matériau imperméable à l'eau.
6. Une composition selon la revendication précédente 5, caractérisée en ce que le matériau imperméable
à l'eau est choisi dans le groupe comprenant: acide laurique, acide myristique et leurs mélanges.
10. 7. Une composition selon l'une quelconque des revendications précédentes, caractérisée en ce que la
composition comprend de plus un électrolyte.
8. Une composition selon la revendication 7, caractérisée en ce que l'électrolyte est le sulfate de sodium.
15. 9. Une composition selon l'une quelconque des revendications précédentes, caractérisée en ce que le pe-
roxyacide organique est un diperoxyacide.
10. 10. Une composition selon la revendication 9, dans laquelle le diperoxyacide est l'acide 1,12-diperoxydodé-
canedioïque.
20. 11. Une composition selon l'une quelconque des revendications 1 à 8, caractérisée en ce que le peroxyacide
organique possède une liaison amide polaire dans la chaîne hydrocarbonée.
25. 12. Une composition selon l'une quelconque des revendications 1 à 8, caractérisée en ce que le peroxyacide
organique est un acide alkylsulfonylperoxycarboxylique.
13. Une formulation détergente, de blanchiment, de nettoyage et/ou de désinfection comprenant une compo-
sition de blanchiment selon l'une quelconque des revendications précédentes.

30 **Revendications pour l'Etat contractant suivant : ES**

1. Un procédé de préparation d'une composition de blanchiment écoulable, comprenant un peroxyacide or-
ganique solide, sensiblement insoluble dans l'eau, en suspension stable dans un milieu aqueux qui
contient au moins deux polymères dans lequel le premier polymère est une ou plusieurs gommes natu-
relles et le second polymère est choisi dans le groupe comprenant l'alcool polyvinyle, un ou plusieurs
35 dérivés de cellulose, et leurs mélanges.
2. Un procédé selon la revendication 1, caractérisé en ce que le premier polymère est la gomme xanthane.
3. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le second po-
lymère est un ou plusieurs éthers de cellulose.
40. 4. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le second po-
lymère est choisi dans le groupe comprenant: méthylcellulose, méthylhydroxypropylcellulose, méthylhy-
droxybutylcellulose, hydroxyéthylcellulose et carboxyméthylcellulose.
45. 5. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le peroxyacide
organique comprend de plus un matériau imperméable à l'eau.
6. Un procédé selon la revendication 5, caractérisé en ce que le matériau imperméable à l'eau
est choisi dans le groupe comprenant: acide laurique, acide myristique et leurs mélanges.
50. 7. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la composition
comprend de plus un électrolyte.
8. Un procédé selon la revendication 7, caractérisé en c qu l'électrolyte est le sulfate de sodium.
55. 9. Un procédé selon l'une quelconqu des revendications précédentes, caractérisé en ce que le peroxyacid
organique est un dip roxyacid .

10. Un procédé selon la revendication 9, dans lequel le diperoxyacide est l'acid 1,12-diperoxydodécanedioïque.
- 5 11. Un procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que le peroxyacide organique possède une liaison amide polaire dans la chaîne hydrocarbonée.
12. Un procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que le peroxyacide organique est un acide alkylsulfonylperoxycarboxylique.
- 10 13. Utilisation de la composition obtenue par le procédé selon l'une quelconque des revendications 1 à 12 en tant que formulation détergente, de blanchiment, de nettoyage et/ou de désinfection.

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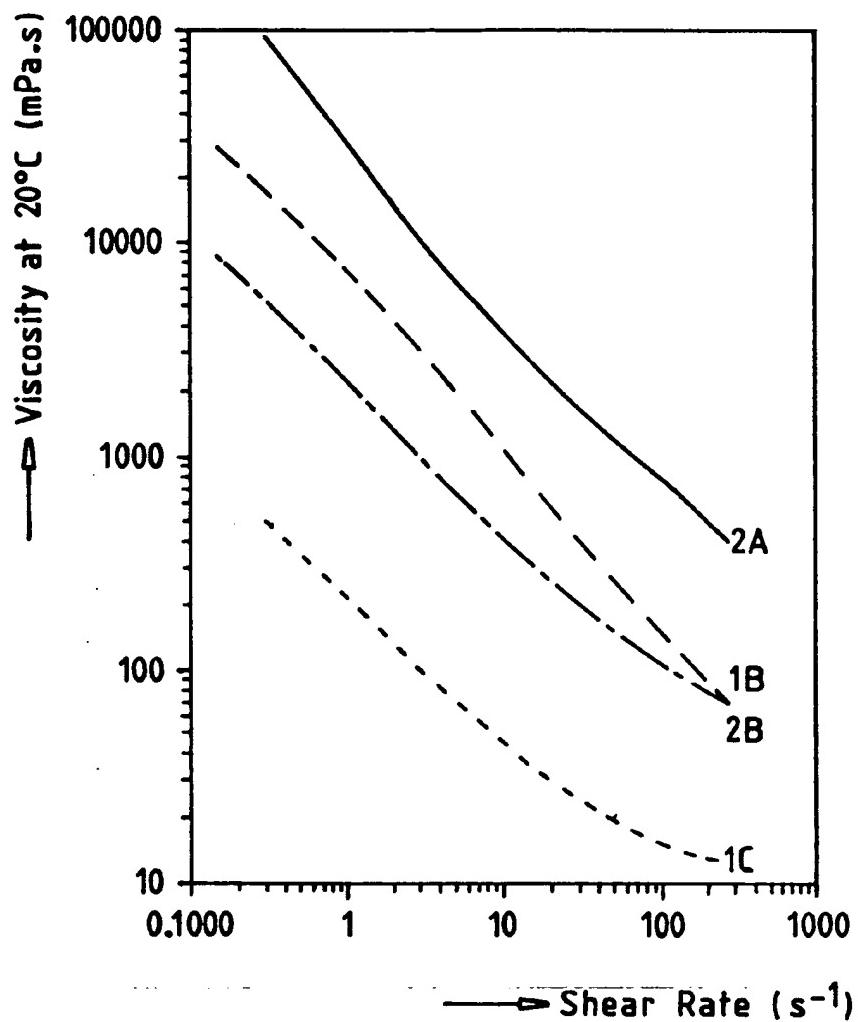
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